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ETCH PITS IN PYROLYTIC GRAPHITE

TECHNICAL REPORT NO. WAL TR 130.5/1

BY

ARAM TARPINIAN
and
GEORGE E. GAZZA

OCTOBER 1960

O.O. PROJECT: TB4-004, MATERIALS FOR HIGH TEMPERATURE USES
D/A PROJECT: 5B93-32-004

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Metallography
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TITLE

ETCH PITS IN PYROLYTIC GRAPHITE

ABSTRACT

The observation of pits in pyrolytic graphite after ion bombardment etching is described and their similarity to dislocation etch pits is speculated. Evidence of etch pit multiplication in the form of slip line segments and low angle tilt boundaries is presented.

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REPORT APPROVED
Date 26 Oct 60
WAL Board of Review
Chairman WGW

INTRODUCTION

In contrast to metals, the effect of microstructure on the properties of graphitic materials has not been investigated sufficiently to demonstrate which features are most significant. It has been shown in the case of metals and other crystalline materials that the nature of the substructures plays an extremely important role in determining the physical properties of the material. Various techniques such as "decorating" and etch pitting have been used to reveal these substructures in materials. Transmission electron microscopy of thin sections has also been utilized by observing the interference patterns produced by the transmission of the electron beam through the lattice imperfections.

In the case of graphites, the only attempts to identify the substructures have been by transmission electron microscopy. A number of electron microscope observations have been made[1,2,3,4] which are reported to be direct evidence of dislocations in graphite. Although there is no reason to believe that graphite is so perfect that it is free of dislocations, the concept of dislocations in graphite is received by many with some skepticism. However, Grenall's work (Reference 3) with the transmission electron microscopy of graphite thin sections showing the movement of dislocation lines induced by the thermal energy provided by the electron beam is quite convincing. The electron microscope work by Dawson and Follett, (Reference 4) showing edge dislocations in the basal plane consisting of two half planes, is also convincing, since one would expect that the atomic arrangement in the hexagonal layer plane would require that two rows of atoms be removed to form the edge dislocation and still maintain the compatibility of the lattice (see Figure 1).

The authors have no knowledge of any published work reporting the use of etch pit techniques and light microscopy for revealing the substructures of graphites. Perhaps the reason for this lack is the fact that until recently there has been little interest in revealing graphite microstructures for metallurgical-type studies. The experience and know-how derived from the study of metal microstructures can be usefully applied to graphite as has already been done in many other nonmetallic and ceramic-type materials. A desire to apply metallographic principles and techniques to graphite prompted our earlier investigations in this area. During the course of these studies, cathodic etching techniques[5] were found to be quite superior to chemical etching[6] for both pyrolytic graphites and graphitized cokes.

Pyrolytic graphite is the term used to describe the graphite deposit derived from the high temperature (> 2000°C) pyrolysis of organic vapors on hot surfaces. The most common raw material used today is methane gas, although there are numerous other organic compounds that will undergo similar pyrolysis reactions. Graphite layers are built up on a hot substrate by the continuous deposition of carbon resulting from the pyrolysis of the organic vapor. The orientation of the crystallites (grains) is such that the basal (00.2) plane lies more or less parallel to the surface of the substrate. Due to the peculiarities of the growth process, the basal planes are bowed with varying degrees of curvature, giving rise to a conical geometry to the grain structure when viewed parallel to the (00.2) plane.

Graphitized cokes are those graphites that are produced by the heat treatment (> 2000°C) of molded or extruded mixtures of petroleum coke particles and pitch or resin binder. The high temperature heat treatment graphitizes both the binder and the coke filler, resulting in a porous body consisting of fairly randomly oriented graphite crystallites held together by a graphitic pitch or resin bond.

The purpose of this paper is to report some recent work using cathodic etching techniques to reveal the substructures in pyrolytic graphite. Pyrolytic graphite was chosen in lieu of graphitized coke because of its closer approach to single crystal behavior due to the preferred orientation of the grain structure. Etch pit arrays have been observed which we believe may be direct evidence of dislocation sites.

EXPERIMENTAL PROCEDURE

In the case of graphites, chemical etching presents a problem because of the relative inertness of graphite with respect to chemical reaction. The choice of chemical reactions for etching is limited to three types: oxidation, formation of lamellar compounds, and carbide formation at high temperatures. Of the three classes, oxidation seems to be the most feasible for use as a means of etching, since the reaction product is gaseous and does not require removal or solution away from the underlying structure.

In previous work by the authors (Reference 6), a mixture of potassium dichromate - phosphoric acid was found to be the most promising oxidizing etchant for graphite. Subsequent work (Reference 5) showed that cathodic etching (ion bombardment) was much more satisfactory. Consequently, cathodic etching techniques were used in the work reported in this paper.

Pyrolytic graphite specimens were sectioned in a transverse manner so that the basal planes are viewed on edge. The sectioned surface was polished, using standard metallographic polishing techniques, and cathodically etched with argon ions. Details of the construction and operation of the cathodic etching apparatus are given in Reference 5. In general, satisfactory etching was accomplished within a half hour, using a voltage drop from 3000-4500 volts at 5-10 ma/cm^2. A constant leak of argon at 20 μ of H_g was maintained during etching so that continuous evacuation of the etching chamber could be accomplished without depletion of the argon supply.

RESULTS AND DISCUSSION

Examination of the etched pyrolytic graphite surfaces using light microscopy revealed conical etch pits in arrays reminiscent of those that have been observed in other materials. Figures 2 through 6 show some of the etch pit arrays that have been observed. All photographs are oriented such that the basal plane runs horizontal across the page.

Figures 2 and 3 show linear arrays of etch pits in the form of slip line segments. Microcracks predominantly along the basal planes are also seen. The interruption of what appears to be slip at a grain boundary is shown in Figure 3. Figure 4 shows the initiation of slip at the tip of microcracks along the basal planes. The occurrence of single pits lining up to form what appears to be low angle tilt boundaries is seen in Figures 5 a and b.

Whether or not mechanical polishing prior to etching is responsible for the observed structures has not been resolved at present. It is more likely that due to the anisotropic behavior of the graphite crystal lattice, thermal expansion in the $\underline{c}$ and $\underline{a}$ axes differs to such an extent as to create thermal stresses in the deposited layers (during high-temperature deposition and during cooling after deposition) which are high enough to initiate plastic flow and propagate microcracks.

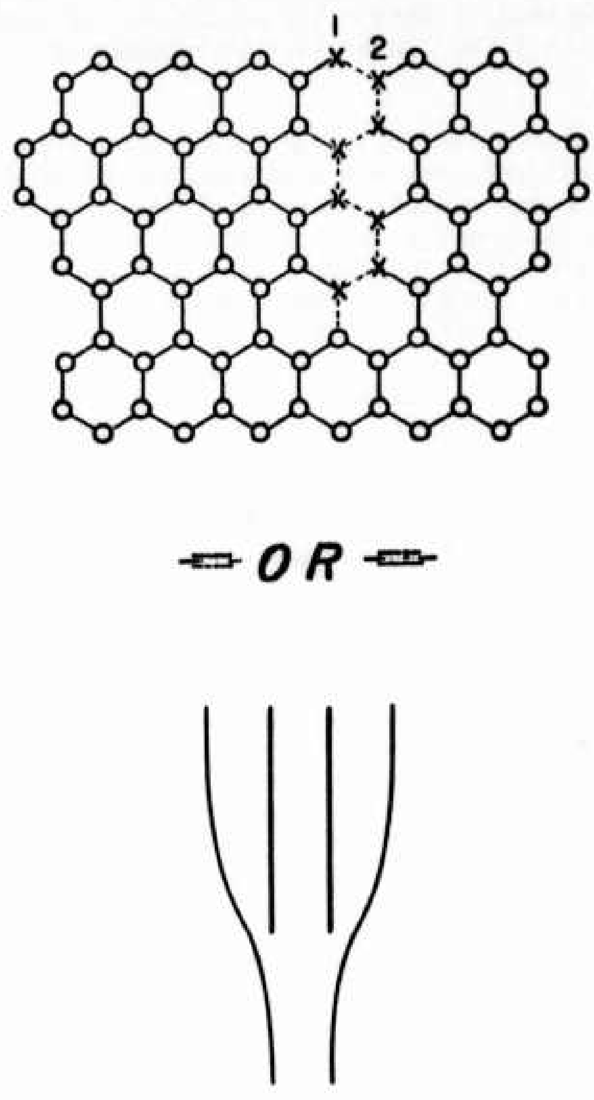
Nevertheless, the purpose of this paper is only to report an etching technique which has been successful in producing preferential attack in the form of etch pits in the surface of pyrolytic graphite. This technique has previously been used for etching graphitized petroleum cokes (Reference 5). A type of pitting was also observed on these materials and explained on the basis that they may be due to the sublimation of impurities during the high temperature heat treatment of the coke. These recent observations with pyrolytic graphite suggest that the pitting observed in the graphitized petroleum coke might be explained in terms of dislocation sites. A comparison of the graphitized petroleum coke structures with those of pyrolytic graphites shows numerous similarities. The similarity between the wavy and bowed lines seen in graphitized coke microstructures and in pyrolytic graphites suggests that the same growth mechanism responsible for the pyrolytic graphite structures is responsible for those seen in graphitized cokes. Figure 6 is a photomicrograph of a graphitized petroleum coke particle showing pitting along the curved basal planes.

SUGGESTIONS FOR FURTHER WORK

Since this investigation was of an exploratory nature, the significance of the results lies in the fact that it has revealed the existence of substructures in graphite which might be explained in terms of dislocation theory.

An obvious extension of this work would be the controlled application of stress to the pyrolytic graphite in order to determine whether there is motion of the etch pit sites due to the stress. This movement of etch pit sites would be expected if they represented dislocation sites.

The question should be resolved as to whether the mechanical polishing of the specimen prior to etching has created a cold worked layer. An attempt should be made to remove the polished layer by chemical means. Perhaps the oxidizing solution of potassium dichromate - phosphoric acid (Reference 6) used previously for etching graphites can be modified and used as an electropolishing chemical for this purpose.



ATOMIC MODEL OF EDGE DISLOCATION IN GRAPHITE[3]

X - DENOTES MISSING ATOMS

FIGURE I

CATHODIC ETCH 2000X

FIGURE 2: MULTIPLICATION OF ETCH PITS WHICH FORM SLIP LINE SEGMENTS (INDICATED BY ARROWS)

CATHODIC ETCH 2000X

FIGURE 3: INTERRUPTION OF SLIP AT THE GRAIN BOUNDARY INDICATED BY ARROW

CATHODIC ETCH 2000X

INITIATION OF SLIP AT THE TIP OF MICRO-CRACKS ALONG THE BASAL PLANE (INDICATED BY ARROWS)

FIGURE 4

a

CATHODIC ETCH b 2000X

LOW ANGLE TILT BOUNDARIES ALONG THE BASAL PLANE

FIGURE 5

CATHODIC ETCH 2000X

PITTING ALONG THE BASAL PLANES OF A GRAPHITIZED PETROLEUM COKE

FIGURE 6

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